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2. HIGH STORAGE DENSITY
3. EXPLORATION OF NEW MATERIALS
4. OPTIMIZATION OF STORAGE AND READOUT
5. IDENTIFICATION OF THE DATA STORAGE MECHANISM
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Final Performance Report

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"Development of Molecular Glasses for Use as Media for High-Density Optical Memory Based on Multi-Photon Absorption"

Objective: The objective of this project was the development of a class of organic materials that we have discovered into practical media for high-density optical data storage based upon multiphoton absorption (MPA).

Background: The materials we investigated for data storage include molecular glasses and epoxy resins, and have the benefits of being inexpensive and readily available. It is also simple to modify the materials chemically to alter their physical and chemical properties.

MPA involves the simultaneous absorption of two or more photons, none of which individually has sufficient energy to cause an electronic transition in a molecule. However, through collective interaction of n photons, such an event can occur. Because the absorption is non-resonant until the final step, the absorption probability is proportional to the laser intensity to the power of the number of photons involved in the process. As a result, MPA can be localized within the focal volume of a laser beam that has been focused through a microscope objective. By controlling the position of the focal volume in three dimensions, different regions of the sample can be addressed.

The materials that we have developed do not fluoresce initially. However, 3-photon absorption of near-infrared radiation leads to a localized photochemical event that renders the materials fluorescent. The fluorescence of the photochemical product can then be read out by 2-photon absorption of near infrared radiation. Because writing of data is a 3-photon process and readout a 2-photon process, readout can be accomplished at considerably lower laser intensities.

Major Accomplishments:

- *Robust Data Storage*. The fact that readout employs considerably lower laser intensities is a very important feature of the process, as it allows data to be read out at intensities that neither harm the existing data nor cause further photochemical changes in the material. As a result, we have been able to read stored data millions of times without causing significant deterioration (Fig. 1). The ability to make millions of reads nondestructively makes these materials suitable for high-density storage. However, it is also essential that the data be robust over time. We have been able to demonstrate stability of data stored at ambient temperature for over 3 years, and once our laboratory is fully set up at University of Maryland we will once again look at the samples. We fully expect that there will have been no significant degradation of the data since we moved in June, which places the stability time at over 4 years.

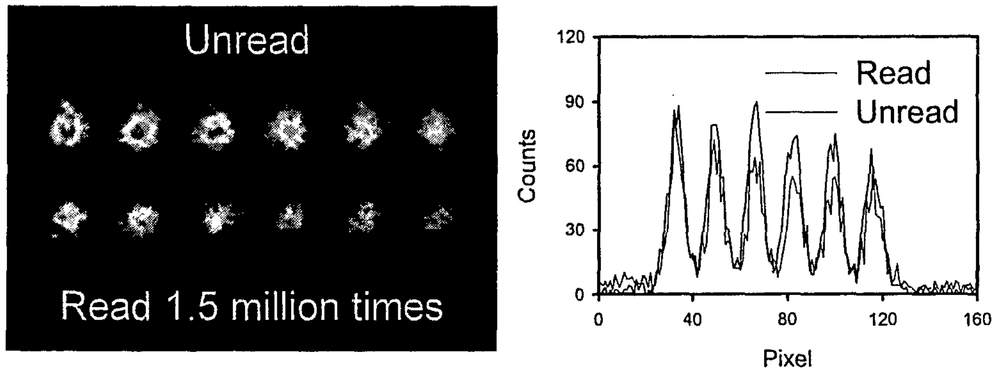

Figure 1. The top line of data was written and then not read until this image was obtained. The lower line of data was read 1.5 million times before this image was taken. As can be seen from the slices through the centers of the rows of data, photobleaching of the data is minimal, as is the increase in the background counts.

- *High storage density.* We initially demonstrated storage densities in the range of 1 GB/cm^2. Subsequent work has improved upon this by nearly an order of magnitude, and considerably more progress is possible.

- *Exploration of new materials.* The ability to store data efficiently depends up a number of material parameters. For instance, in molecular glasses we have found that it is essential to be near, but below, the glass transition temperature for writing to be efficient. Based on such observations, we have successfully made chemical modifications to storage materials to change physical parameters to promote the storage process.

- *Optimization of storage and readout.* A broadly tunable Ti:sapphire laser purchased with a DURIP grant was used to explore the optimal wavelengths, powers and pulse durations for data storage and retrieval. We were able to optimize data storage by moving to a wavelength to the blue of the standard 800 nm. Similarly, by moving to the red we were able to read out data at higher powers (and therefore faster) without writing additional data. We are still exploring the dependence of the writing process on pulse energy and pulse length.

- *Identification of the data storage mechanism.* Extensive experiments have pointed to the bisphenol diether moiety of the compounds employed as the key chemical structure for data storage. Identifying

the storage mechanism is more challenging, as we create a very small amount of photoproduct in the focus of the laser beam. However, we were able to prove that the mechanism involved radical formation followed by reaction with oxygen. In fact, as an interesting sidelight to this project, we were able to show that bisphenol diether methacrylate resins can be polymerized by MPA without the need for a photoinitiator, another clear sign that the photoproduct is generated via a radical intermediate. Our belief is that the radical intermediate undergoes geminate recombination at low viscosities, and cannot convert to the final fluorescent product if the viscosity is too high. Thus, temperatures right below the glass transition are ideal in reaching a happy medium between these effects.

- *Pulse measurement.* As mentioned above, we have worked to understand how the laser pulse length affects writing and readout. Shorter laser pulses are optimal for writing, in order to drive the three-photon absorption process. In the case of readout, longer pulses can help to prevent unintended writing. However, making such measurements in a reliable manner requires being able to determine the laser pulse length at the focal point of the objective. In the past, this has been accomplished with interferometric techniques, which are inconvenient when the pulse length is many optical cycles. We have developed an in-line, non-interferometric autocorrelation and cross-correlation system that is simple to use and allows for rapid pulse length measurement at the sample position.

Personnel Supported: Amity King, graduate student; Mariko Okamoto, graduate student; Christopher LaFratta, graduate student; Christopher Olson, graduate student; Juliet Znovena, graduate student; John Fourkas, PI.

Publications:

"Efficient and Robust Multiphoton Data Storage in Molecular Glasses and Highly-Crosslinked Polymers," Christopher E. Olson, Michael J. R. Previte and John T. Fourkas, *Nature Mater.* **1**, 225 (2002).

"In-line Autocorrelator for Nonlinear Optical Microscopy," Christopher N. LaFratta, Juliet Znovena and John T. Fourkas, to be submitted to *Optics Express*.

"Optimization of Multiphoton Data Storage and Readout in Molecular Glasses," Amity Ziegler and John T. Fourkas, to be submitted to *Chemistry of Matierals*.

Interactions/Transitions: The work being supported under this grant has been presented in the following talks:

"Seeing and Shaping the Microscopic World with Multiphoton Absorption" Department of Physics, Boston College, 2/26/02.

"Seeing and Shaping the Microscopic World with Multiphoton Absorption" Department of Chemistry, University of Maryland, 4/11/03.

"Seeing and Shaping the Microscopic World with Multiphoton Absorption" Environmental Molecular Sciences Institute, Columbia University, 7/16/03.

"Seeing and Shaping the Microscopic World with Multiphoton Absorption" Department of Physics, Emory University, 9/19/03.

"Seeing and Shaping the Microscopic World with Multiphoton Absorption" Department of Chemistry, Arizona State University, 10/6/03.

"Seeing and Shaping the Microscopic World with Multiphoton Absorption" Modern Optics and Spectroscopy seminar, MIT, 10/28/03.

"Making Things With Light" Materials Science Institute seminar, University of Oregon, 11/07/03.

"Making Things With Light" Department of Chemistry, University of Maryland, 1/28/04.

"Making Things With Light" Department of Chemistry, University of Southern California, 2/12/04.

"Making Things With Light" Department of Physics, University of Massachusetts, Lowell, 4/15/04.

"Making Things With Light" Spire Corporation, Bedford, MA, 9/14/04.

"Making Things With Light" Department of Chemistry, University of North Carolina, Chapel Hill, 9/22/04.

"Making Things With Light" Boston Regional Inorganic Chemistry Association Meeting, Chestnut Hill, MA, 9/23/04 (invited).

"Making Things With Light" Earthlink Senior Technical Staff Seminar, Atlanta, GA, 10/20/04.

"Making Things With Light" Department of Electrical and Computer Engineering, University of Maryland, 10/21/04.

"Making Things With Light" ACS Undergraduate Day, Boston University, 11/6/04.

"Making Things With Light" Department of Chemistry, University of Maine, 4/19/05.

"Toward the Fabrication of Functional Microdevices Using Multiphoton Absorption," 13th NSF Workshop on Materials Chemistry and Nanoscience, 10/28/05-10/31/05.

"Toward the Fabrication of Functional Microdevices Using Multiphoton Absorption," Laboratory for Physical Science, University of Maryland, 2/15/06.

"Making Things with Light," Institute for Physical Science and Technology, University of Maryland, 2/20/06.

New inventions, discoveries, or patent disclosures: "Apparatus and Materials for Three-Dimensional Optical Data Storage and Retrieval," US 6,998,214 (2006).

Press coverage of grant activity:

Chemical & Engineering News, November 25, 2002

Chemical & Engineering News Research Highlight, December 2002

Photonics Spectra, January 2003

Materials Today, January 2003

Dozens of Web sites, including *Science Now* and *HighTech Magazine*.

Honors and Awards: Named a Fellow of the American Physical Society; Senior editor, *Journal of Physical Chemistry*, 7/02-present; Named Fellow of the American Association for the Advancement of Science, 2005.